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⑤④ Elastomer based adhesive compositions.

⑤⑦ A substantially solvent-free adhesive composition consists essentially of an elastomer and tackifier, a metal oxide and, optionally, a plasticizer. The elastomer is selected from the group consisting of polar elastomers and unsaturated elastomers which have at least 5 mole percent unsaturation, said elastomer being a non-crystalline elastomer or an elastomer which has a slow rate of crystallization such that after a time period of at least 100 hours has elapsed following subjecting the elastomer to a temperature of 70°C for 30 minutes, the elastomer has a room temperature Shore A hardness of less than 60. The adhesive compositions can be formed into a shaped article, such as of a tape, film, sheet or tubular sleeve, if desired. The compositions have high adhesive strength for bonding together a variety of substrates. The adhesive is particularly useful with a dimensionally recoverable article, such as a shrinkable sleeve, to bond the recovered sleeve to a substrate such as an electric cable.

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This invention relates to a substantially solvent-free adhesive composition which may be used as a sealant between elongate substrates such as electrical cables and polymeric sleeves recovered thereon.

5 Dimensionally recoverable articles such as tubular and wraparound sleeves are well known for use in enclosing elongate substrates such as pipes or cables and, in particular, cable joints or splices, and can be sealed to the substrate, if desired, for example
10 using a mastic or hot melt adhesive for heat-recoverable sleeves.

 Dimensionally recoverable articles which do not require heat to effect recovery are also well known. Such articles are typically formed of an elastomeric
15 sheet or tube held in an expanded state by a restraining means which can be removed or separated from the elastomeric member to permit it to recover to the unexpanded state. Such articles are also used to enclose elongate substrates and it is also desirable
20 that the recovered article be sealed to the substrate. Generally, contact adhesives have been used for this purpose. The contact adhesive is a solvent based adhesive which can be placed on at least part of the substrate, generally before the recoverable sleeve is
25 placed in position about the substrate. The contact adhesive can be coated on the interior surface of the sleeve, but this has been found inconvenient.

 Solvent based contact adhesive used in this manner and applied to the substrate only provides a relatively
30 weak adhesive bond. Further, the adhesive has a

paste-like consistency making it difficult to apply it uniformly to the substrate. Non-uniform application can lead to inadequate sealing of the recovered sleeve to the substrate. This in turn creates leak paths
5 through which water can migrate. This is particularly undesirable when the substrate enclosed by the sleeve is a joint between electric cables.

This invention provides an adhesive composition, preferably in the form of a self-supporting tape,
10 sheet, film or sleeve for convenient application to an elongate substrate, the flow and adhesive characteristics of the adhesive composition making it particularly suitable for use with a dimensionally recoverable sleeve to seal the recovered sleeve to
15 the substrate.

This invention accordingly provides an adhesive composition consisting essentially of a substantially solvent-free admixture of:

(a) 100 parts of an elastomer selected from the
20 group consisting of polar elastomers and unsaturated elastomers which have at least 5 mole percent unsaturation, said elastomer being a non-crystalline elastomer or an elastomer which has a slow rate of crystal-
25 lization such that after a time period of at least 100 hours has elapsed following subjecting the elastomer to a temperature of 70°C for 30 minutes, the elastomer has a

room temperature Shore A hardness of less than 60;

(b) 5 to 200 parts of a tackifier;

5 (c) 0.5-20 parts of an oxide of a metal of Group Ia, IIa, IIb, IVa or VIb of the Periodic table; and

(d) 0-100 parts of a plasticizer;

said adhesive composition exhibiting a flow of at least 30% at 97°C under a compressive load of 50 grams.

10 Another aspect of the invention provides a method of enclosing an elongate substrate which comprises:

15 (a) positioning a dimensionally recoverable sleeve over at least a portion of said substrate;

(b) interposing a layer of an adhesive composition between said substrate and said article, said adhesive composition consisting essentially of:

20 (i) 100 parts of an elastomer selected from the group consisting of polar elastomers and unsaturated elastomers which have at least 5 mole percent unsaturation, said elastomer being a
25 non-crystalline elastomer or an

5 elastomer which has a slow rate of crystallization such that after a time period of at least 100 hours has elapsed following subjecting the elastomer to a temperature of 70°C for 30 minutes, the elastomer has a room temperature Shore A hardness of less than 60;

(ii) 5 to 200 parts of a tackifier;

10 (iii) 0.5-20 parts of an oxide of a metal of Group Ia, IIa, IIb, IVa or VIb of the Periodic table; and

(iv) 0-100 parts of a plasticizer;

15 said adhesive composition exhibiting a flow of at least 30% at 97°C under a compressive load of 50 grams.

(c) causing said article to dimensionally recover into intimate contact with said adhesive layer.

20 Yet another aspect of this invention provides a dimensionally recoverable article comprising:

(a) an expanded elastomeric sheet maintained in the expanded state;

(b) a restraining means for maintaining said

5 (i) 100 parts of an elastomer selected from the group consisting of polar elastomers and unsaturated elastomers which have at least 5 mole percent unsaturation, said elastomer being a non-crystalline elastomer or an elastomer which has a slow rate of crystallization such that after a time period of at least 100 hours has elapsed following subjecting the elastomer to a temperature of 70°C for 30 minutes, the elastomer has a room temperature Shore A hardness of less than 60;

15 (ii) 5 to 200 parts of a tackifier;

(iii) 0.5-20 parts of an oxide of a metal of Group Ia, IIa, IIb, IVa or VIIb of the Periodic table; and

(iv) 0-100 parts of a plasticizer;

20 said adhesive composition exhibiting a flow of at least 30% at 97°C under a compressive load of 50 grams.

25 Polar elastomers which can be used include, for example, polychloroprene (also referred to herein as neoprene), epichlorohydrin elastomers, chlorinated polyethylene, chlorosulfonated polyethylene, propylene oxide elastomer, nitrile elastomers, such as acrylonitrile/ butadiene copolymers, acrylic elastomers, such

as butyl acrylate homo- and copolymers, ethylene/
acrylic acid copolymers, polysulfides, elastomeric
vinyl acetate copolymers and polyurethanes. Par-
ticularly preferred elastomers are neoprene and
5 epichlorohydrin/ ethylene oxide copolymers. The
neoprene used should be one of the so called slow
crystallization grades, such as neoprene WK, WD, WRT,
TRT or GRT, which are commercially available grades of
neoprene.

10 Unsaturated elastomers which can be used include,
for example, polybutadiene, polyisoprene, butadiene and
isoprene copolymers such as styrene-butadiene copoly-
mers, styrene-butadiene-styrene block copolymers, and
styrene isoprene-styrene block copolymers, natural
15 rubber and the like. The unsaturated elastomer should
contain at least about 5 mole percent unsaturation,
preferably at least about 10 mole percent unsaturation.

The elastomer used in the adhesive composition of
this invention is a slow crystallizing or non-crystal-
20 line elastomer. The rate of crystallization of an
elastomer can be determined by a procedure which
involves heating a sample of the elastomer at 70°C for
about 30 minutes. The sample is then cooled to room
temperature. The Shore A hardness at room temperature
25 is determined at elapsed time intervals. If after
about 100 hours the room temperature Shore A hardness
is 60 or less the elastomer is referred to herein as a
slow crystallizing elastomer. Preferred elastomers for
use in preparing the adhesive composition of this
30 invention have a room temperature Shore A hardness of
less than 60 after about 200 hours, and in particular
after about 350 hours, following the heat treatment.

5 The adhesive composition contains 5-200 parts
by weight per 100 parts of elastomer of a tackifier.
Tackifiers that can be used include, for example, rosin,
modified rosin, rosin derivatives such as rosin salts or
rosin esters, hydrocarbon resins, polymerized petroleum
hydrocarbons, polyterpenes, phenolic resins, terpene
phenolic resins, coumarone-indene resin and the like.
The amount of tackifier added to the elastomer depends
on the particular elastomer and tackifier used and on
10 the desired end use of the adhesive.

 The tackifier can be present in an amount of
about 5 parts by weight to about 200 parts by weight,
preferably from about 30 parts by weight to about 100
parts by weight per 100 parts by weight of elastomer.

15 The adhesive composition preferably contains up
to about 20 parts by weight per 100 parts of elastomer
of a metal oxide. The metal oxide is preferably an
oxide of a Group Ia, IIa, IIb, IVa or VIb metal of the
Periodic Table. (The Periodic Table referred to herein
20 is that found in the "Handbook of Chemistry and
Physics" 50th edition, 1969-1970, published by The
Chemical Rubber Company). Particularly preferred are
the oxides of lead, zinc or magnesium or mixtures of
such oxides.

25 The amount of metal oxide added can be up to
about 20 parts by weight per 100 parts by weight of
elastomer. Preferably the metal oxide is present in an
amount of about 0.5 to about 10 parts by weight and
most preferably in an amount of about 1 to about 6
30 parts by weight per 100 parts by weight of elastomer.

The adhesive composition can also contain a plasticizer. The plasticizer can be present in amounts ranging from 0 to 100 parts by weight per 100 parts by weight of the elastomer. Preferably, the plasticizer
5 will be present in an amount from about 10 to about 80 parts by weight, particularly from about 30 to about 70 parts by weight per 100 parts by weight of the elastomer. The amount of plasticizer used will depend on the particular elastomer used in the adhesive com-
10 position also on the nature of the plasticizer.

Typical plasticizers which can be used include, for example, chlorinated paraffins, esters such as dioctyl phthalate or dioctyl adipate, polymeric esters, petroleum oil including aromatic naphthenic and
15 paraffinic oil, and liquid or low molecular weight polymers and elastomers such as low molecular weight polychloroprene, epichlorohydrin polymers, nitrile polymers, polysulfides, polyisoprene, polyisobutylene, polybutene, butyl rubber, polyurethane and the like.

20 The particular plasticizer selected and the amount used will depend on the elastomer of the adhesive composition. The plasticizer selected should be compatible with the elastomer and promote the desired properties of the adhesive.

25 The adhesive compositions can contain other additives, for example, antioxidants, acid scavengers, flame retardants, fillers, processing aids and the like.

The adhesive compositions are substantially solvent-free. By substantially solvent-free is meant that no more than about five percent of a solvent is present in the composition. The compositions are generally used in the form of a tape, sheet, film, tubular sleeve or other desired shape. The adhesive compositions have particularly high adhesive strength and can be used with a variety of substrates. Substrates which can be joined using the adhesive compositions of this invention include polymers and elastomers, such as polyethylene, polyvinyl chloride, neoprene, metals such as lead, copper, and the like.

The adhesive compositions can be formed and processed using conventional techniques and equipment. The adhesive components can be added to a mixer such as a two-roll mill, a Sigma mixer, twin-screw extruder of the type suitable for use with elastomeric materials, and the like. The adhesive formulation can be shaped into the desired configuration, such as a tape or sheet, by extrusion, compression molding, calendaring, or the like. The adhesive can be laminated to one of the substrates to be bonded. In some embodiments it may be convenient to coextrude a polymeric substrate and the adhesive composition forming an integral structure.

The adhesive compositions have high adhesive strength and can be applied to a variety of substrates as mentioned above. It is believed that the flow characteristics of the adhesive compositions of this invention contribute to this high adhesive strength. The ability of the compositions to flow permits

adequate wetting of the substrates by the substantially solvent-free adhesive compositions. Flow of the adhesive also results in uniform distribution of the adhesive forming a water-tight seal between the substrates. It is believed that the ability of the compositions to flow indicates that the adhesive compositions are not highly cross-linked.

It has been found that the adhesive compositions should flow at least about 30%, preferable at least about 50%, at 97°C. The flow characteristics are measured, as described in more detail hereinafter, using a thermomechanical analyzer. A sample of the elastomer is placed under a compressive load and the change in thickness of the sample measured. This measurement indicates the degree to which the elastomer flowed under pressure. If the flow is less than about 30% at 97°C, the composition is considered to have insufficient flow to perform satisfactorily as an adhesive.

20

EXAMPLES

Each composition listed in Table I was prepared by adding the components one at a time to a 3 inch roll mill, heated to a temperature of 50 to 80°C. The composition was mixed for a period of time sufficient to obtain a good dispersion, generally about 30-60 minutes. The components and the amount used in each composition in parts by weight is given in Table I.

Flow Determination

The flow characteristics of each adhesive composition was determined using a Thermomechanical Analyzer, commercially available from Perkin Elmer Corporation. A sample 1/4" in diameter and 0.05 inch thick was placed in the Thermomechanical Analyzer on the floor of the quartz sample tube. The quartz probe was placed in contact with the sample and a 50 gram load was placed on the probe. The sample was heated from -30°C to +120°C at a heating rate of 5°C per minute. Changes in sample thickness were measured at intervals as the sample was heated under the applied load. Flow (97°C) was determined as the percent change in sample thickness, at 97°C, i.e. the ratio of the change in sample thickness to the original sample thickness, multiplied by 100.

The results are shown in Table I.

Adhesive Strength Testing

The compositions were tested to determine their adhesive strength.

A 60 gram sample of each composition was pressed into a slab, 6 inches by 6 inches by 0.050 inch, using a press set at 100°C for 8 minutes at 20,000 pounds pressure. The slab was removed from the hot press and placed in a cold press at 25°C for 5 minutes at 20,000 pounds.

5 The sample was tested for adhesive strength by cutting the slabs into 1 inch strips. The strips were wrapped over a portion of an electric cable having a neoprene outer jacket. A dimensionally recoverable tubular article comprising an expanded neoprene sheet held in the expanded state with a solvent releasable external hold-out layer, was positioned over the adhesive strips wound on the cable. Solvent was applied to release the recoverable neoprene sheet from the hold-out allowing it to recover and shrink into contact with the adhesive coated cable portion. After about 24 hours the cable portion was cut into 1 inch samples. The electric wires were removed and the sample was slit open. The neoprene jacket of the cable and the recovered neoprene layer were grasped in an Instron and pulled apart in a T-peel test. The adhesive strength in pounds per linear inch (pli) is given in Table II. The samples were pulled at room temperature at a rate of 50 millimeters per minute. The results are given in Table II. Also noted was whether the sample failed cohesively, that is failure of the adhesive layer, or adhesively, that is failure at the interface between the adhesive and either of the neoprene layers.

25 Certain of the adhesive compositions were also tested, as above, to bond a recovered neoprene article to a copper tube and to an electric cable with a cross-linked polyethylene outer jacket. In each instance, the adhesive strength was tested using a rolling drum peel test. In this test the tube or cable

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was not slit open but mounted on a suitable drum. A cut was made through the recovered neoprene sleeve and the adhesive layer and the force needed to separate the adhesive from the copper tube or polyethylene jacket was determined. Whether the failure was cohesive or adhesive was noted.

The Hydrin-based adhesives were tested by pressing a layer of the adhesive between two ethylene/vinyl acetate copolymer (containing 18% vinyl acetate) sheets to be bonded together at room temperature under contact pressure for 2 minutes. The bonded structure was then subjected to a T-peel adhesive test as described above.

The results of the adhesive strength testing is shown in Table II.

In Table I the following notations are used:

Neoprene WRT - a slow crystallizing grade of neoprene (commercially available from Du Pont)

Hydrin 200 - (an epichlorohydrin-ethylene oxide copolymer commercially available from Goodrich Chemical Company)

ZnO - Zinc Oxide

MgO - Magnesium Oxide

CaCO₃ - Calcium Carbonate

SP553 - a terpene phenolic resin (commercially available from Schenectady Chemical Company)

PRJ551 - a reactive phenolic resin (commercially available from Schenectady Chemical Company)

Stabelite Ester 10 - Rosin ester (commercially
available from Hercules, Inc.)
Neoprene FB - a low molecular neoprene (commer-
cially available from Du Pont)
5 Hydral - Alumina trihydrate (commercially avail-
able from Alcoa)
Octamine - an amine antioxidant produced by
reacting diphenylamine with diisobuty-
lene (commercially available from
10 Vanderbilt Chemical Company)
Sb₂O₃ - Antimony oxide
Chlorowax 70L - high viscosity grade chlorinated
paraffin wax
Chlorowax 40 - low molecular weight chlorinated
15 paraffin wax
A097 - Polyketone resin (commercially available
from 40 Chemical Company)
Hycar 2216X2 - a liquid epichlorohydrin homo-
polymer (commercially available
20 from B.F. Goodrich Chemical
Company)
Agerite Resin D - polymerized 1,2-dihydro-2,2,4-
trimethylquinoline, an antiox-
idant (commercially available
25 from B.F. Goodrich Chemical
Company)

TABLE I

Parts by Weight

| Composition | A | B | C | D | E | F | G | H | I | J | K | L | M | N | O | P | Q | R | S | T |
|--------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Neoprene WRT | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | --- | --- | 100 | 100 | 100 |
| Hydrin 200 | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | 100 | 10 | 0 | --- | --- |
| Neoprene PB | 55 | 55 | 55 | 55 | 55 | --- | --- | 55 | 55 | 55 | 55 | 55 | 55 | 55 | 55 | --- | --- | 55 | 55 | 55 |
| Chlorowax 70L | --- | --- | --- | --- | --- | --- | 55 | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Chlorowax 40 | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | 30 |
| Hycar 2216X2 | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | 50 | 50 | --- | --- | --- |
| ZnO | 3 | 3 | 3 | 3 | 3 | 3 | 3 | --- | --- | --- | 1 | --- | --- | 1 | --- | --- | --- | 2 | 2 | 3 |
| MgO | 3 | 3 | 3 | 3 | 3 | 3 | 3 | --- | --- | --- | --- | 2 | 3 | 3 | 5 | 3 | 3 | 2 | 2 | 3 |
| CaCO ₃ | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | 5 | 5 | 50 | 50 | --- |
| SP553 | --- | 35 | --- | --- | 70 | 35 | 35 | 35 | 35 | --- | 35 | 35 | 35 | 35 | 35 | --- | --- | --- | 35 | 35 |
| FRJ551 | --- | --- | 35 | --- | --- | --- | --- | --- | --- | 35 | --- | --- | --- | --- | --- | --- | 35 | --- | --- | --- |
| Stabelite Ester 10 | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | 35 | --- | --- |
| A097 | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | 35 | --- | --- | --- | --- |

TABLE I (cont.)

Parts by Weight

| Composition | A | B | C | D | E | F | G | H | I | J | K | L | M | N | O | P | Q | R | S | T |
|--------------------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Hydral | 35 | 35 | 35 | --- | --- | 35 | 35 | 35 | 35 | 35 | 35 | 35 | 35 | 35 | 35 | 25 | 25 | --- | --- | 35 |
| Sb ₂ O ₃ | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | 15 |
| Octamine | 3 | 3 | 3 | 3 | 3 | 3 | 3 | --- | 3 | 3 | 3 | 3 | 3 | 3 | 3 | --- | --- | 2 | 2 | 3 |
| Agerite Resin D | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | 2 | 2 | --- | --- | --- |
| Flow at 97°C (%) | --- | --- | 70 | --- | --- | --- | 80 | --- | 100 | 100 | 100 | 100 | 100 | 100 | 77 | 77 | 100 | --- | --- | --- |

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TABLE II

| Composition | Substrates | Test Method | Adhesive Strength (PLI) | Mode of Failure* |
|-------------|---|--------------|----------------------------|------------------|
| A | Neoprene/Neoprene | T-Peel | 15.5 | AF |
| B | Neoprene/Neoprene | T-Peel | 20.7 | CF |
| C | Neoprene/Neoprene Neoprene/Polyethylene Neoprene/Copper | T-Peel | 15.9 | CF |
| | | Drum Drum | 22.9 14 | CF/AF CF/AF |
| D | Neoprene/Neoprene | T-Peel | 11.3 | AF |
| E | Neoprene/Neoprene | T-Peel | 21.7 | CF/AF |
| F | Neoprene/Neoprene | T-Peel | 22.2 | CF/AF |
| G | Neoprene/Neoprene | T-Peel | 12.4 | CF |
| H | Neoprene/Neoprene | T-Peel | 5.4 | CF |
| I | Neoprene/Neoprene | T-Peel | 14.3 | CF |
| J | Neoprene/Neoprene | T-Peel | 16.1 | CF/AF |
| K | Neoprene/Neoprene | T-Peel | 11.6 | CF |
| L | Neoprene/Neoprene | T-Peel | 14 | CF |
| M | Neoprene/Neoprene | T-Peel | 10.3 | CF |
| N | Neoprene/Neoprene | T-Peel | 16.1 | CF/AF |

TABLE II cont.

| Composition | Substrates | Test Method | Adhesive Strength (PLI) | Mode of Failure* |
|-------------|----------------------------|-------------|----------------------------|------------------|
| O | Neoprene/Neoprene | T-Peel | 11.3 | CF |
| | Neoprene/Polyethylene | Drum | 19.8 | CF |
| | Neoprene/Copper | Drum | 11.5 | CF |
| P | both Ethylene/Vinylacetate | T-Peel | 8.1 | CF |
| Q | both Ethylene/Vinylacetate | T-Peel | 14.3 | CF |
| R | Neoprene/Neoprene | T-Peel | 7.1 | CF |
| S | Neoprene/Neoprene | T-Peel | 8.7 | CF |
| T | Neoprene/Neoprene | T-Peel | 5.9 | CF |

* Mode of Failure - AF= adhesive failure
CF= cohesive failure

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As mentioned above, the adhesive compositions of this invention are particularly useful for use with dimensionally recoverable articles to bond the recovered article to a substrate. The dimensionally recoverable article can be a dimensionally heat-recoverable article, such as heat-shrinkable polymeric tubing and wraparound sleeves which are well known. For example, see U.S. Patents Nos. 3,086,242, 3,455,336 and 4,207,364 (the disclosures of which are incorporated herein by reference) for a description of typical articles of this type. Such dimensionally heat-recoverable articles are frequently lined with a mastic or hot melt adhesive. The adhesive compositions of this invention can be used with such heat-recoverable articles. The adhesive composition is interposed between the recoverable article and the substrate. The adhesive can be in the form of a tape, sheet, film, sleeve or laminated to the recoverable article.

The adhesive compositions are particularly suitable for use with dimensionally recoverable articles which do not require heat to cause recovery thereof. The flow and adhesive characteristics of the adhesives of this invention are such that heat is not required to cause the adhesive to flow and wet the substrate or otherwise activate the adhesive. Dimensionally recoverable articles which do not require heat to effect recovery are typically elastomeric articles held under tension in an expanded state. When the means holding the elastomeric member in the expanded state is removed, released or otherwise separated from the expanded elastomeric member, the elastomeric member

recovers to its original unexpanded state. The means holding or retaining the elastomeric member in the expanded state can be an internal means such as that disclosed in U.S. Patent No. 3,515,798, but is preferably on external means such as that described in U.S. Patents Nos. 4,070,746, 4,135,553, 4,179,320, 4,287,012, and U.K. Patent No. 1,556,677.

10 The adhesive compositions can be used with dimensionally recoverable articles of this type in the same manner as described above with heat-recoverable articles. The adhesive and flow characteristics of the compositions are such that the adhesive composition flows and wets the inner surface of the recoverable article and the substrate without application of heat.
15 The adhesive compositions can be used at temperatures of 20°C and lower depending on the particular elastomer used in the composition. The adhesive can be laminated to the recoverable elastomeric sheet or can even be coextruded with the elastomeric sheet as it is being
20 produced, if desired.

Dimensionally recoverable articles of this type comprise a recoverable sleeve of elastomeric material and a suitable restraint or hold out means. The sleeve can be an expanded tube of elastomeric material or can
25 be a longitudinal slit tube held under tension. The elastomeric sleeve can be virtually any desired material possessing elastomeric recovery properties. Suitable elastomers include materials such as natural and synthetic polyisoprenes, polybutadiene, styrene-butadiene rubber (SBR), butadiene-acrylonitrile rubber,
30 polychloroprene (Neoprene), butyl rubber, polysulfide,

silicone rubber, urethane rubber, polyacrylate, epichlorohydrin homo- and copolymers, propylene oxide rubber, fluorosilicone rubber, fluorocarbon rubber, chlorosulfonated polyethylene, chlorinated polyethylene, ethylenepropylene rubber, nitroso rubber and phosphonitrilic rubber. The properties of the sleeve are, to a large extent, dependent upon the intended use of the sleeve. Thus, if the sleeve is to be used primarily as an electrical insulation, its electrical properties will be of primary importance. On the other hand, if the sleeve will be subjected to much physical abuse, it may be necessary to provide a sleeve which has toughness, good flame resistance, good solvent resistance, etc. For high voltage uses, it may be desirable to have a sleeve which has been made semi-conductive by dispersing large amounts of suitable fillers or conductive particles in the sleeve or possesses resistance to tracking and/or erosion.

The adhesive composition used should be compatible with the elastomeric material of the recoverable articles. For example, a neoprene based adhesive can be used with a neoprene recoverable sleeve. Such similarity between the sleeve and adhesive is not, however, essential as the adhesive compositions of this invention are compatible with numerous substrates. The adhesive composition should also be compatible with the substrate to be covered. When the substrate is an elastomeric cable, the adhesive composition can contain additives to improve certain properties such as fire retardancy, electrical properties and the like.

CLAIMS

1. An adhesive composition consisting essentially of a substantially solvent-free admixture of:

5 (a) 100 parts of an elastomer selected from the group consisting of polar elastomers and unsaturated elastomers which have at least 5 mole percent unsaturation, said elastomer being a non-crystalline elastomer or an elastomer which has a slow rate of crystal-
10 lization such that after a time period of at least 100 hours has elapsed following subjecting the elastomer to a temperature of 70°C for 30 minutes, the elastomer has a room temperature Shore A hardness of 60 or less;

(b) 5 to 200 parts of a tackifier;

15 (c) 0.5-20 parts of an oxide of a metal of Group Ia, IIa, IIb, IVa or VIb of the Periodic table; and

(d) 0-100 parts of a plasticizer;

20 said adhesive composition exhibiting a flow of at least 30% at 97°C under a compressive load of 50 grams.

2. A composition in accordance with Claim 1, wherein said adhesive composition is in the form of a tape, sheet, film or sleeve.

25 3. A composition in accordance with Claim 2, wherein said adhesive composition is in the form of a self-supporting tape, sheet, film or sleeve.

4. A composition in accordance with any of the preceding claims, wherein said elastomer is slow crystallizing neoprene.
5. A composition in accordance with any of Claims 1 to 3, wherein said adhesive composition is an epichlorohydrin/ethylene oxide copolymer.
6. A composition in accordance with any of the preceding claims, wherein said tackifier is present in an amount in the range of from about 30 to about 100 parts by weight per 100 parts by weight of elastomer.
7. A composition in accordance with any of the preceding claims, wherein said tackifier is selected from the group consisting of rosin, modified rosin, hydrocarbon resins, polymerized petroleum hydrocarbons, polyterpenes, comarone-indene resin.
8. A composition in accordance with any of Claims 1 to 6, wherein said tackifier is a phenolic resin.
9. A composition in accordance with any of Claims 1 to 6, wherein said tackifier is a terpene-phenolic resin.
10. A composition in accordance with any of Claims 1 to 6, wherein said tackifier is a rosin derivative.
11. A composition in accordance with any of the preceding claims, wherein said metal oxide is present in an amount in the range of from about 0.5 to about 10 parts by weight per 100 parts by weight of the elastomer.

12. A composition in accordance with any of the preceding claims, wherein said metal oxide is selected from the group consisting of the oxides of zinc magnesium and lead.
- 5 13. A composition in accordance with any of Claims 1 to 11, wherein said metal oxide is zinc oxide.
14. A composition in accordance with any of Claims 1 to 11, wherein said metal oxide is magnesium oxide.
- 10 15. A composition in accordance with any of the preceding claims, wherein said plasticizer is present in an amount in the range of from about 10 to about 80 parts by weight per 100 parts by weight of elastomer.
- 15 16. A composition in accordance with any of the preceding claims, wherein said plasticizer is a low molecular weight neoprene.
- 20 17. An adhesive composition consisting essentially of 100 parts by weight of slow crystallizing neoprene, 30 to 100 parts by weight of a terpene phenolic tackifier, 0.5 to 10 parts by weight of metal oxide selected from the group consisting of zinc oxide, magnesium oxide, and mixtures thereof and 10 to 80 parts by weight of a plasticizer selected from the group consisting of low molecular weight neoprene, chlorinated paraffin wax and mixtures thereof.
- 25 18. A dimensionally recoverable article comprising:
- (a) an expanded elastomeric sheet maintained in the expanded state;

(b) a restraining means for maintaining said elastomeric sheet in the expanded state; and

5 (c) a layer of adhesive composition on the surface of said elastomeric sheet which is in the direction of dimensional recovery of the sheet, said adhesive composition consisting essentially of:

10 (i) 100 parts of an elastomer selected from the group consisting of polar elastomers and unsaturated elastomers which have at least 5 mole percent unsaturation, said elastomer being a non-crystalline elastomer or an elastomer which has a slow rate of crystallization such that after a time period of at least 100 hours has elapsed following subjecting the elastomer to a temperature of 70°C for 30 minutes, the elastomer has a room temperature Shore A hardness of less than 60;

(ii) 5 to 200 parts of a tackifier;

25 (iii) 0.5-20 parts of an oxide of a metal of Group Ia, IIa, IIb, IVa or VIIb of the Periodic table; and

(iv) 0-100 parts of a plasticizer;

said adhesive composition exhibiting a flow of at least 30% at 97°C under a compressive load of 50 grams.

19. A method of enclosing an elongate substrate
5 which comprises:

(a) positioning a dimensionally recoverable article over at least a part of said substrate;

10 (b) interposing a layer of an adhesive composition between said substrate and said article, said adhesive composition consisting essentially of;

15 (i) 100 parts of an elastomer selected from the group consisting of polar elastomers and unsaturated elastomers which have at least 5 mole percent unsaturation, said elastomer being a non-crystalline elastomer or an elastomer which has a slow rate of crystallization such that after a time period
20 of at least 100 hours has elapsed following subjecting the elastomer to a temperature of 70°C for 30 minutes, the elastomer has a room temperature Shore A hardness of less than 60;

25 (ii) 5 to 200 parts of a tackifier;

(iii) 0.5-20 parts of an oxide of a metal of Group Ia, IIa, IIb, IVa or VIb of the

Periodic table, and

- 5 (iv) 0-100 parts of a plasticizer;
 said adhesive composition exhibiting a flow
 of at least 30% at 97°C under a compressive
 load of 50 grams.
- (c) causing said article to recover dimen-
 sionally into intimate contact with said
 adhesive layer.



European Patent
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EUROPEAN SEARCH REPORT

Application number

| DOCUMENTS CONSIDERED TO BE RELEVANT | | | EP 82306904.2 |
|--|--|--|---|
| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | CLASSIFICATION OF THE APPLICATION (Int. Cl. 7) |
| A | <p><u>US - A - 3 595 821</u> (S. SPECTOR)</p> <p>* Abstract; column 2, lines 11-36; column 3, lines 6-48; column 5, lines 11-28; column 9, lines 24-55; claims 1-7 *</p> <p>--</p> | 1,7-10 12,13 | <p>C 09 J 3/12</p> <p>C 09 J 7/00</p> <p>B 29 C 27/20</p> <p>B 32 B 31/00</p> <p>C 08 L 11/00</p> |
| A | <p><u>US - A - 3 965 061</u> (D.L. BASH et al.)</p> <p>* Abstract; table 1; claims 1-2 *</p> <p>--</p> | 1,7-10 12,13 | |
| A | <p><u>DE - A1 - 2 531 085</u> (UZIN WERK GEORG UTZ)</p> <p>* Page 3, line 19 - page 7, line 17; page 10, lines 1-8; page 13, lines 2-5; claims 1,4,5 *</p> <p>----</p> | 1-3,7, 8,12, 13 | <p>TECHNICAL FIELDS SEARCHED (Int. Cl. 7)</p> <p>C 09 J</p> <p>B 29 C</p> <p>B 32 B</p> <p>C 08 L 11/00</p> |
| The present search report has been drawn up for all claims | | | |
| Place of search VIENNA | | Date of completion of the search 09-03-1983 | Examiner KAHOVEC |
| <p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone</p> <p>Y : particularly relevant if combined with another document of the same category</p> <p>A : technological background</p> <p>O : non-written disclosure</p> <p>P : intermediate document</p> <p>T : theory or principle underlying the invention</p> <p>E : earlier patent document, but published on, or after the filing date</p> <p>D : document cited in the application</p> <p>L : document cited for other reasons</p> <p>& : member of the same patent family, corresponding document</p> | | | |

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